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Inorganic constituents formed during small-scale gasification of poultry litter: A model based study

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ABSTRACT

Europe's vast poultry industry requires a proper waste management in order to comply with environmental regulations. As a result, poultry litter represents a potential fuel candidate for thermal conversion technologies since it is an available source. Therefore, a process simulation for the gasification of poultry litter is examined in this study. This process integrates a fluidised bed gasifier with a gas turbine with the aim of generating combustibles gases for energy production. The system allows the treatment of waste with the additional benefit of energy generation. A small-scale system (200 kWe) installed on-site the biomass source shows to be suitable for a poultry farm to avoid the litter transportation to centralised plants. Among the by-products generated during gasification, such as NO_x, SO_2, and tar, ash represents a potential risk since bed agglomerates can lead to loss of fluidisation and alkali vapours in the product gases can increase rates of hot corrosion on turbine surfaces. This work presents the partition of the most problematic inorganic species in order to assess the feasibility of the system and identify the optimum parameters to minimise the vaporisation of inorganics. It was found that low ER values produced low HCl emissions and good process efficiencies but released very high SO_2 emissions.

1. Introduction

The use of traditional methods for disposal of poultry litter is no longer desirable, due to environmental and legislative constraints. These constraints have encouraged the development of alternative methods of disposal, which also can produce a valuable fuel from poultry litter. These methods include thermo-chemical conversion technologies such as pyrolysis, combustion and gasification [1]. In particular, small-scale gasification eliminates the transportation costs of litter as a result of on-site processing. Furthermore, the gasification process integrated with a gas turbine (GT) can be used to generate electricity and directly run the farm operations in order to achieve sustainable farming.

Gasification produces hot combustible gases and bottom ash containing particles of unburned material [2]. Ash consists of inorganic species such as alkali oxides and salts and its composition varies depending on the type of fuel. Typically, the analysis of ash constituents is reported in the form of oxides. However, ash is composed of different species and has been classified in three main groups that include [3]:

- salts ionically bound,
- inorganics bound organically to the carbonaceous material, and
- minerals present in the fuel structure and foreign material from biomass harvesting.

In general, potassium, sodium, and chlorine are the inorganics more problematic in fluidised bed (FB) gasification. The presence of ash in FB gasifiers represents a potential risk, since bed agglomerates can lead to loss of fluidisation (defluidisation) and alkali vapours in the product gases can increase rates of hot corrosion on turbine surfaces in integrated systems [4]. Defluidisation during FB operation has been attributed to the formation of a thin sticky glass coating around the bed particles, followed by almost instantaneous defluidisation. From Scanning Electron Microscopy (SEM) combined with Energy Dispersed X-ray analysis (EDX) analyses, it was found that agglomerates were not homogeneous for olive pomace ash; melted parts showed a potassium to calcium ratio >1, whilst for not melted parts the ratio was <1 [5]. Consequently, combustion turbine manufacturers recommend a total fuel-gas alkali content of less than 50 ppb which ensures the safe operation of the machines [6].

Positive effects of alkalis have also been acknowledged, that is, char biomass has been attributed with catalytic effects. Wood impregnated with K_2CO_3 (8 wt.%) showed to reduce the amount of phenolic tar components, polycyclic aromatic hydrocarbons, furans and ketones by a factor of 5–10 [7]. NaOH and Na_2CO_3 additives have been studied on lignin pyrolysis and gasification. In addition, potassium and calcium were reported to accelerate the gasification rate of biomass char (from Japanese cypress) loaded with $Ca(OH)_2$ and K_2CO_3 at higher temperatures of 1173–1223 K [8]. Steam gasification of pine wood-derived char impregnated with different ash-components before pyrolysis was evaluated, and catalytic activities were ranked as: $KNO_3 > KHCO_3 \approx K_2CO_3 \approx KOH > NaOH > CaO > K_2HPO_4 > KBr > KCl >$ no additive $> Fe_2O_3$; it was found that wood impregnated with wood ash increased char reactivity by a factor of 15 [9].

Limited comprehensive research on the release of alkali and alkaline earth metallic species (AAEMs) during biomass gasification is found in

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the literature [10–12]. Most reports available are only concerned on the measurement of gaseous species such as NH_3, H_2S, HCN and COS. The main reasons are the large variety of biomass feedstock and the difficulties related to experimentally measuring inorganics. Among these experimental difficulties are: sampling condensable species by trapping media requires sample point located in high temperature zones, accurate bed mass balance due to bed agglomeration, reliable mass balances due to bed material attrition and entrainment, and corrosion avoidance of pipes or traps [13]. Traditionally, alkalis sampling involved passing the sampled gas through a series of impingers bottles to capture alkali species, followed by off-line analysis using analytical methods such as atomic emission spectrometry or liquid chromatography; for that reason, the measurements are average values over a period of time.

Few on-line, time-resolved measurement studies are found in the literature. It was reported that signals from HCl^+, KCl^+, $NaCl^+$, K^+ and Na^+ were successfully measured by molecular beam mass spectrometry (MBMS) during fluidised bed gasification at temperatures of 1073, 1173 and 1273 K with the oxygen/fuel ratio of 0.5 [14]. In MBMS, the sample gas is introduced into a vacuum chamber where a molecular beam is formed and analysed by a mass spectrometer. HCl was well detected in three of the four biomass samples. For clean wood, the relatively high potassium to chlorine ratio promoted the bulk of chlorine as KCl. Miscanthus released the highest amount of H_2S at 1173 K, due to its low Ca/S ratio. Other employed method for measuring alkalis concentration, using a pilot-scale bubbling fluidised bed (BFB) gasifier (5 kW_{th}) of wood pellets, was surface ionization detection (SID) [15]. Experiments were performed using an air/fuel ratio of 0.44 and the reactor bed temperature of around 1028 K. The measurements were achieved by the development of a sampling and dilution setup that allowed to quantity alkali emissions from feedstock containing high amounts of alkalis. Finally, on-line alkali species measurements were conducted for steam gasification of three pelletized biomass fuels using excimer laser-induced fragmentation fluorescence (ELIF) in a BFB reactor [16]. Average concentrations for potassium were 140 to 350 ppb, and for sodium 1.7 to 60 ppb. From pyrolysis and gasification experiments on three types of biomass, it was reported that 53–76% of alkali metal and 27–40% of alkaline earth metal evaporated during pyrolysis of char at 1173 K, and 12–34% and 12–16%, respectively, for steam gasification of char [10].

Due to experimental difficulties, alkali partition has been studied through modelling work using FactSage software. The release of alkali metals and chlorine during combustion of Danish straw, Swedish wood and sewage sludge under pressurised conditions were studied by equilibrium calculations. Sixteen elements were considered for the chemical system which resulted in 611 species (143 gas, 94 liquid and 374 solid). The main alkali containing species identified were: $K_2Si_4O_{9(liq)}$, $KCl_{(g)}$ and $KOH_{(g)}$ for straw combustion, $KCl_{(g)}$, $K_2SO_{4(g)}$ and $KOH_{(g)}$ for wood gasification at >1100 K, and $HCl_{(g)}$, $NaCl_{(g)}$ and $NaOH_{(g)}$ for sewage sludge combustion [17]. Other study used spruce and pine sawdust for FB gasification. The calculations involved fewer than 1500 species. At 1173 K, they found that ten elements (Zn, Hg, Cd, and Pb in their elemental form, and N, S, Cl, Se, F, Sb in hydride or oxyhydride form) were completely volatilised, ten elements (Ca, Si, Al, P, Ti, Fe, Cr, Mn, Ba and Mg in oxide form) remained entirely in the condensed phase, and five elements (As, K, Ag, Na and B) were semi-volatile [13].

Poultry litter is the waste resulting from poultry rearing activities that consists of a mixture of manure, waste bedding, and waste food. Poultry litter can be a challenging fuel due to its composition; it contains a significant amount of ash, reported values are between 15.7 and 28.8 wt.% [18], which consists of inorganic species such as alkali oxides and salts. The high content of nutrients, such as nitrogen, potassium, calcium, phosphorous and sulphur, is due to the excreta contained in the litter [19].

In order to make gasification a potential option for waste disposal and generation of energy, issues concerning ash formation should be addressed. Therefore, this study investigates the fate of inorganic constituents produced during gasification. A small-scale plant of 200 kW_e is proposed to treat poultry litter on-site, which is integrated with a gas turbine to generate the electricity consumed during poultry operations. Due to the difficulties of sampling inorganics and the lack of open-literature using poultry litter as fuel, this study is based on an equilibrium model. Based on the main alkali species identified experimentally and through comprehensive modelling work, this work proposes the inclusion of a minimum number of species which will allow the evaluation of the partition of the most problematic inorganics in FB gasification: potassium, sodium, and chlorine. The optimal operating parameters are determined in order to avoid the vaporisation of inorganic species which might pose adverse effects on the gas turbine. Effects of changing the equivalence ratio (ER) and moisture content of poultry litter are evaluated in order to determine optimal conditions, gas compositions, calorific values and efficiencies.

2. Methods

A model based on chemical equilibrium was employed as presented in a previous work, which corresponds to case 6; details of the 200 kW_e

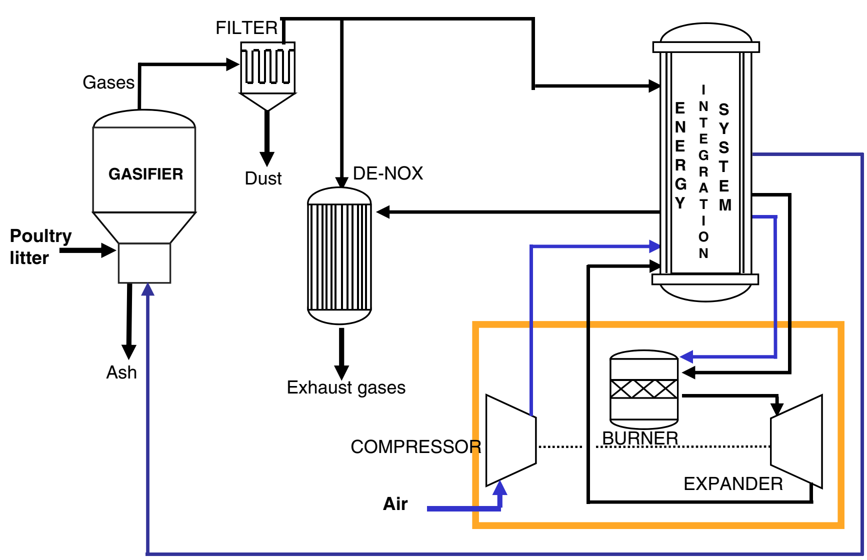

Fig. 1. Schematic diagram of the small-scale process.